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Phosphate test strips
A new equipment for direct soil-phosphate field analysis

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After some years of research a new method for direct soil-phosphate field analysis has been developed at the Archaeological Research Laboratory, Stockholm University. The determination principle is now used by Merck, Germany to produce field kits with pre-impregnated test strips and reagents built on the PMB-method (phosphomolybdenum blue).

Introduction

The fact that human activity increases soil-phosphate content was mentioned by agriculturalists in Egypt as early as 1911. A Swedish agronomist, Olof Arrhenius, was the first to describe a method for, and systematically carry out, soil-phosphate analysis in archaeological mapping (O. Arrhenius 1931; 1935; 1950). First to describe a field application of soil-phosphate analysis was Walter Lorch, Germany, who used a spot-test for field-phosphate mapping and made it possible to carry out interactive field prospecting. It was now possible to use the results in the field and let them guide mapping operations to the optimal area (Lorch 1940; 1941a; 1941b). An improved field spot-test was later described by H. Gundlach, Germany (Gundlach 1961) and I. & S. Österholm, Sweden (Österholm & Österholm 1982).

These methods have been used both to map already known settlements, in attempts to locate boundaries and interpret the activity, and to search actively for unknown settlements. Lately active multi-prospecting methods have become more common. Soil-phosphate analysis has been combined with other geochemical elements and with geophysical methods like magnetometry, electromagnetic and electric measurements and ground-penetrating radar.

A new test strip, developed at the Archaeological Research Laboratory, Stockholm University, is an attempt to improve the applicability of soil-phosphate field analysis. We hope that phosphate field analysis in combination with other geochemical and geophysical field methods in interactive prospecting will be more common. The measurements and insights gained from varying methods will allow the best possible results to be obtained.

Method

Phosphorus is essential to plants, and any lack of it inhibits growth and delays ripening. It is found in soils as organic P, inorganic P and soil-solution P. Soil-solution P is often found as orthophosphate ions (PO_4^{3-}). Most phosphates are strongly fixed to the soil and not available to plants. Plants take up phosphorus from soil-solution phosphates, which is available to the plants, and agricultural methods aim to analyse only that fraction. It may be difficult to define what is available to plants since different soils and different plants behave differently in the phosphate cycle. Archaeological use of soil-phosphate analysis should take into consideration also the organic and inorganic P fractions. Phosphorus from the organic fraction in plants or animal tissues will, after decomposition, become available as a substrate for soil organisms and micro-organisms. It will then either be mineralized and added to the inorganic fraction or incorporated into the micro-organisms as a part of the organic fraction. If the soil-phosphate cycle is disturbed by anthropogenic influence, the organic fraction will decrease in relation to total P, because part of it is mineralized, and both the soil-solution P and the inorganic fraction will increase (Madanov & Voykin 1966). Some research also suggests that phosphate can be mineralized at high temperature due to fire or in a fermentation process in dung heaps or waste heaps (B. Arrhenius 1990). By searching for such

Figure 1. Site location.

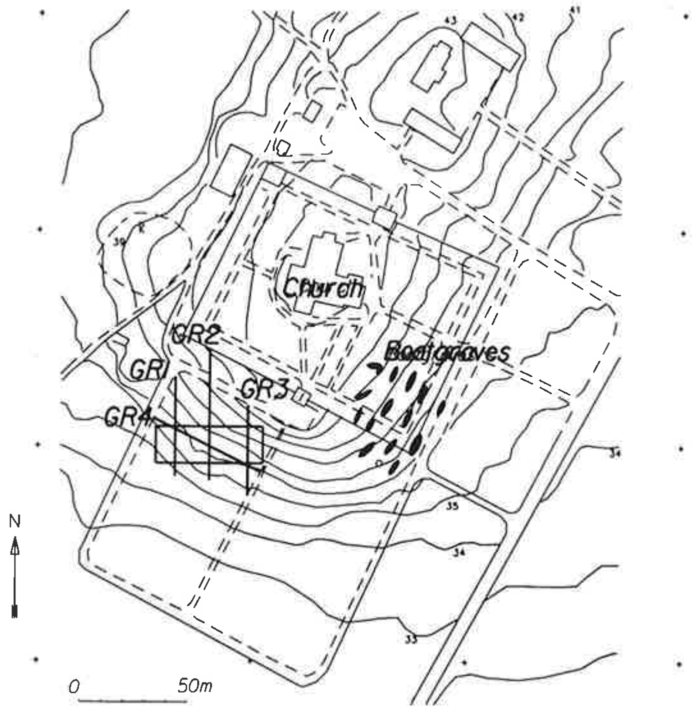

Figure 2. Map showing Vendel church, the boatgraves and in bold lines the survey area and the radar profiling lines.

anomalies soil-phosphate analysis can be used in archaeological prospecting.

In acid solutions orthophosphate ions, PO_4^{3-}, and molybdate ions form molybdo-phosphoric acid, which can be reduced to phosphomolybdenum blue, PMB. The concentration of PMB can be determined photometrically or visually against a colour scale.

The test strips

The determination principle, patented by the author, is now used by Merck, Germany, to produce test strips. In Scandinavia they are sold by KEBO, Stockholm. A reactive zone on the test strip and the solutions in the reagent bottles are prepared with molybenum and a reduction agent. The strips can be used for water, soil and food analysis. One version is part of Merck Reflectoquant system (Merck cat. no. 1.16978, KEBO art. no. 1.9161-0) in which the test strips are measured in a portable reflecting photometer (Merck cat. no. 16970, KEBO art. no. 105.045-0). The other version is part of Merckoquant system (Merck cat. no. 1.10428, KEBO art. no. 6.8335-0) and the test strips are compared visually with a colour scale on the package. There are test strips for other elements available in both systems which make it possible to carry out multi-element prospecting. The description in the phosphate field kits describes how to analyse a liquid. In soil analysis it is necessary first to extract the phosphates from the soil and then to measure the liquid. Users may choose the extraction method and after the extraction let the soil settle before pouring off the liquid. The pH-value must be within the range 4–10. Otherwise, it has to be corrected with sodium hydroxide or sulphuric acid.

• **Reflectoquant** test strip is sold in a package with a tube containing 50 test strips, a bar-code strip for cali-

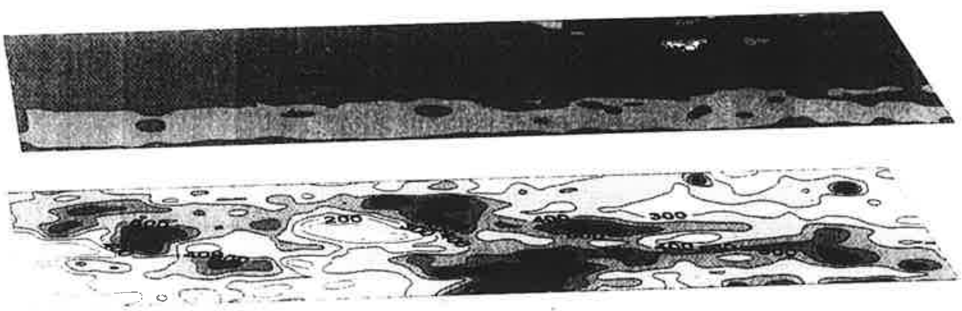

Figure 3. Contour maps showing the distribution of electromagnetic real-component anomalies; contours in ppt (parts per thousand) of the primary field (top), and distribution of soil phosphates (mg P_2O_5/100 g soil).

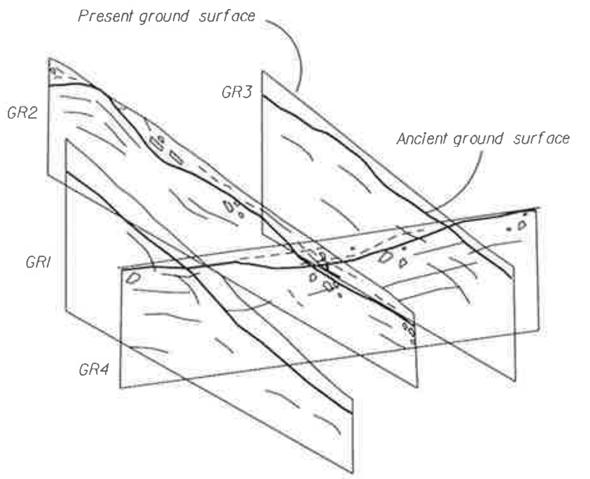

Figure 4. Interpretations of the radargrams GR1–GR4.

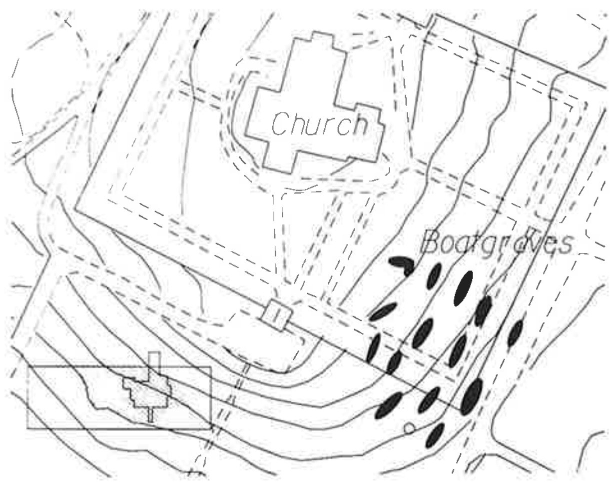

Figure 5. The results of the survey with the survey area and the trench in bold lines. The hatched area is the interpretated cultural layers.

brating the photometer, one reagent bottle and a test vessel. The reagent bottle contains 16% sulphuric acid and in tests at the Archaeological Research Laboratory we have used that solution for the extraction.

Procedure: Take 5 ml water and add 10 drops of the reagent. Add 1 ml soil and swirl for two minutes. Immerse the test strip for 2 s and wait 90 s before measuring in the photometer. The display shows the phosphate content of the liquid and hence the content of the soil is five times higher. Result is given as ppm PO_4^{3-} dissolvable in H_2SO_4. The measuring range for Reflectoquant phosphate is 5–120 ppm PO_4^{3-} in the liquid. Data are digitized and automatically stored in the photometer and can easily be transferred to the field computer for processing in mapping and profiling software.

• **Merckoquant** test strip is sold in a package with a tube containing 100 test strips, one reagent bottle, and a test vessel. In our tests we have used 1.2 M HCl for extraction.

Procedure: Take 5 ml 1.2 M HCl, add 1 ml soil and swirl for two minutes. Immerse the test strip for one second and shake off excess liquid. Put one drop from the reagent bottle on the reactive zone of the test strip and after 15 s shake off excess reagent liquid. Wait 60 s and then compare the colour of the reactive zone with the colour scale on the package. The result shows the phosphate content of the liquid and the content of the soil is five times higher. Result is given as ppm PO_4^{3-} dissolvable in 1.2 M HCl.

The measuring range for Merckoquant phosphate test strip is 10–500 ppm PO_4^{3-} in the liquid. Besides the field kit, a wash bottle and a 1 ml measure for the soil are needed. Ordinary tap water can be used. If necessary, the phosphate content of the water can first be analysed with the test strips.

Hazards

In soil field analysis it is desirable to use a strong acid to get a quick extraction. These methods use sulphuric acid and hydrochloric acid while other phosphate analysis methods use, for instance, citric acid, nitric acid or a lactate solution. Differences in extractors and extraction times are vitally important for the result and for what fraction is analysed and therefore direct comparisons between these various methods are not possible. The methods described here assume volume measurements so the soil mass can vary. If a more accurate method is required the user must dry and weigh the soil in the field. This may prove problematic and it is desirable to have fast and practical methods in field prospecting. We have found volume measurements of the soil samples provide sufficient information to be able to point out places with an increased soil-phosphate content compared with surrounding natural soils.

Material and results

The Archaeological Research Laboratory has used the test strips for field prospecting within two ongoing projects, *Tunagården i Vendel* and SIV (*Svealand in the Vendel and Viking Periods*). We have carried out soil-phosphate analysis with both laboratory and field analysis, first with a spot-test method and since 1994 with the test strips. Phosphate mapping has been combined with electric conductivity measurements using Geonics slingrams and with GPR, ground-penetrating radar.

The purpose for the prospecting was to locate settlements and houses connected to the famous boatgraves at the Vendel church in Vendel parish, Uppland, Sweden (fig. 1). Conductivity measurements with Geonics EM-31 showed interesting anomalies just south of the church. Soil samples from the places with positive anomalies were taken with corers and the phosphate content was measured directly with test strips. The results showed that at certain locations there was a dark-coloured layer with a high content of soil phosphate. Therefore we decided to carry out a multi-prospecting survey on that area. This consisted of a more accurate Geonics EM-38

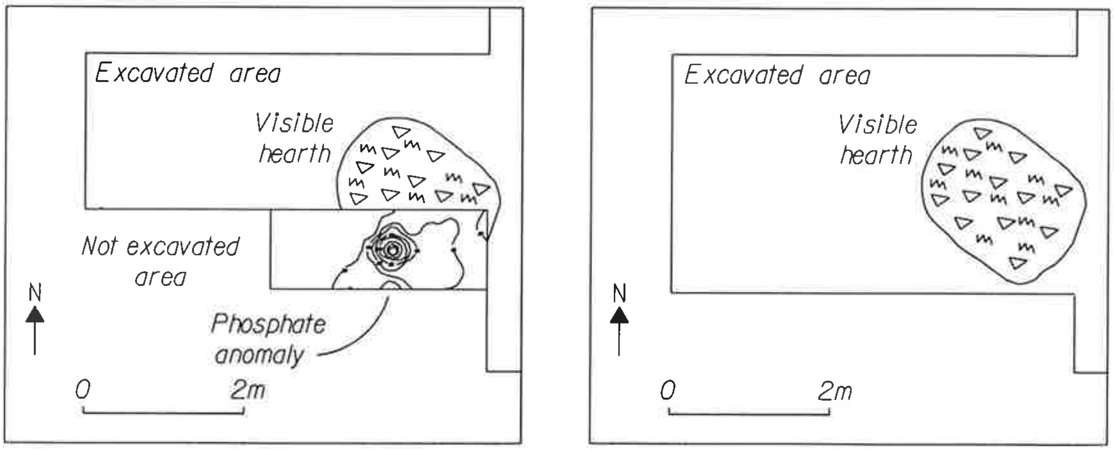

Figure 6. Map showing (left) the partly uncovered hearth and the phosphate distribution just south of the trench. (Right) the whole hearth is visible after further excavation.

for the conductivity mapping, combined with dense soil sampling for phosphate analysis in the laboratory, and profiling using ground-penetrating radar (fig. 2). The results are presented as contour-maps for phosphate and electromagnetic readings (fig. 3) and interpretation of the radargrams (fig. 4). Combined, these methods gave us the possibility to interpret the extension of the cultural layer on the terrace (fig. 5). The excavations so far in the eastern part of the terrace have confirmed our interpretations.

During the excavation a large rectangular hearth was partly uncovered. Between the stones a black, sooty soil with high phosphate content was found. The part of the hearth we uncovered indicated a continuation of the hearth into the unexcavated area. We took soil samples and mapped the area of the indicated continuation in order to test whether the test strips could identify single objects such as hearths. When compared with the results of the extended excavation, the phosphate map proved to indicate accurately the area where such features occured (fig. 6).

Conclusions

In our tests we have found the phosphate test strips to be of great value in field prospecting. Mostly this is because they make it possible to carry out extensive interactive multi-prospecting with geophysical field measurements combined with a direct geochemical field method. We hope that other users also will find them useful. Merck, Germany, is now developing soil applications for other elements, which hopefully will in the future give us a complete archaeological geochemical field kit.

Acknowledgements

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References

Arrhenius, B. 1990. Fosfat och spårämnesanalyser som hjälpmedel vid bebyggelseanalys. *Bebyggelsehistorisk tidskrift* 19, pp. 63–77.

Arrhenius, O. 1931. Die Bodenanalyse im dienst der Archäologie. *Zeitschrift fürPflanzenernährung, Düngung und Bodenkunde* Teil B, 10. Jahrgang, pp. 427–39.

Arrhenius, O. 1935. Markundersökning och arkeologi. *Fornvännen* 30, pp. 65–76.

Arrhenius, O. 1950. Förhistorisk bebyggelse antydd genom kemisk analys. *Fornvännen* 45, pp. 59–62.

Gundlach, H. 1961. Tüpfelmethode auf Phosphat, angewandt in prähistorischer Forschung (als Feldmethode). *Mikrochimica Acta* 5, pp. 735–37.

Lorch, W. 1940. Die siedlungsgeographische Phosphatmethode. *Die Naturwissenschaften* 28, pp. 633–40.

Lorch, W. 1941a. Chemische Spuren im Boden als Zeichen fürherer menschlicher Besiedlung. *Die Umschau in Wissenschaft und Technik* 45, pp. 116–20.

Lorch, W. 1941b. Die Phosphatmethode im Dienste der Vorgeschichtsforschung. *Germanen-Erbea* 6, pp. 55–59, 90–95.

Madanov, P. V. & Voykin, L. M. 1966. Buried soils under Russian fortifications in the 17th and 18th centuries. *Soviet Soil Science Pochvovedniye* No. 9, pp. 999–1004.

Österholm, I. & Österholm, S. 1982. Spot test som metod för fosfatanalys i fält – praktiska erfarenheter, *Riksantikvarieämbetets Gotlandsundersökningen, Arkeologiska skrifter,* Nr 1982:6.